

THE INSTITUTE OF PAPER CHEMISTRY

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February 21, 1986

TO: Fourdrinier Kraft Board Group of the American Paper Institute

Enclosed, for your information and use, is the first progress report for Project 2926-9, Review of Corrosion of Electrostatic Precipitators.

This report reviews the present knowledge of corrosion problem in electrostatic precipitators used in pulp and paper mills. Acid dewpoint corrosion, the principal cause of corrosion damage, is described. Operating variables which affect this corrosion are discussed. Remedies for corrosion, and published corrosion testing methods are outlined. This information will be useful as a reference source and may be used to get an early start on corrosion control through the application of present knowledge. It also identifies directions in which efforts must be exerted to improve our understanding and experience.

If you have any questions, please contact me (414/738-3266) or David Crowe (414/738-3235).

Sincerely,

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RAY/sjb  
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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

REVIEW OF CORROSION IN ELECTROSTATIC PRECIPITATORS

Project 2926-9

Report One

A Progress Report

to

MEMBERS OF THE FOURDRINIER KRAFT BOARD GROUP

January 31, 1986

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REVIEW OF CORROSION IN ELECTROSTATIC PRECIPITATORS

ABSTRACT

Corrosion problems in electrostatic precipitators are reviewed. Acid dewpoint corrosion, the principal cause of corrosion damage, is described. Operating variables which affect this corrosion are discussed. Remedies for corrosion, and published corrosion testing methods are outlined.

## SUMMARY FOR THE NONSPECIALIST

The service lives of electrostatic precipitators are shortened by corrosion. The problems have been identified by a recent TAPPI survey.<sup>1</sup> Problem areas included side walls, outlet vanes, ductwork, access doors, wire weight guide frames, inlet areas, instrument penetrations and bottom pans. Unfortunately, there is a scarcity of information on how to deal with this corrosion. Most of the information deals with electrostatic precipitators in other industries and it is not known if precipitators in the pulp and paper industry have some special problems.

Dewpoint corrosion is the principal form of corrosion. More specifically, this refers to acid dewpoint, the temperature below which sulfuric acid in flue gas condenses onto surfaces. The sulfuric acid forms by reaction of sulfur trioxide gas and water vapor. As temperature decreases below the dewpoint, the rate of buildup of acid increases to a maximum at a temperature about 30 C below the acid dewpoint and this corresponds to the point of maximum corrosion rate. Hydrochloric acid will condense out at some temperature between the sulfuric acid dewpoint and the water dewpoint. When the temperature is reduced further, the water dewpoint is reached. Sweating will occur below the acid dewpoint due to water uptake by the acid, the salt cake and the corrosion deposits. At temperatures below the water dewpoint, sweating will be increased. Corrosion may be intensified under sticky deposit buildups.

Corrosion in electrostatic precipitators may be reduced through the use of higher flue gas temperatures, lower  $\text{SO}_3$  levels (and thus  $\text{H}_2\text{SO}_4$ ) and lower chloride concentrations (to reduce  $\text{HCl}$  in the flue gas). Process changes to reduce sulfidity in the recovery boiler would reduce  $\text{SO}_3$  concentrations.

Operation of the recovery boiler may influence  $\text{SO}_3$  concentrations, too. Design improvements could include better insulation and sealing (to prevent air ingress) and more resistant materials of construction. Adequate velocities must be maintained to prevent buildups. Boiler startup and shutdown procedures are important because temperature cycling must be minimized to prevent condensation. Sootblowing with steam may introduce water which will be absorbed into hygroscopic deposits or stimulate acid formation.

There is good incentive to learn more about corrosion in electrostatic precipitators and identify remedies. There is a need to better define conditions causing corrosion and to find out how to manipulate the process to avoid these conditions. For example, the recovery boiler operation may be operated to optimize flue gas composition, so that corrosion is minimized. Corrosion rates of materials of construction need to be characterized. Instruments and techniques must be developed to assist in this effort. Ultimately, costs of maintenance (and replacement) can be reduced, longer equipment life can be achieved, and lower flue gas temperatures, with attendant heat savings, may be possible.

## INTRODUCTION

Electrostatic precipitators are employed in recovery of salt cake from recovery boiler flue gases and reduction of particulate emissions. Parallel collection plates, 225-250 mm (9-10 inches) apart are supported from the structural shell of the precipitator. Wire or rigid frame ionization electrodes located between the plates are charged to voltage levels of 55-70 kV.<sup>1</sup> They ionize the flue gas and charge the salt cake particles, which then collect on the grounded collecting plates. Dust collected on the plates is periodically removed by mechanical rappers and collected in a black liquor collecting bath or in a dry pan at the bottom of the precipitator.

Electrostatic precipitators may be dry bottom or wet bottom type. The wet bottom design first came into use on direct contact evaporator (DCE) recovery boiler precipitators around 1948. During the 1960's, when efforts to reduce TRS emissions indicated that the principal source of recovery boiler odors was contact of the black liquor and flue gas in the direct contact evaporator, the same was thought to be true for precipitator wet bottoms. The response was the NCE (noncontact evaporator) recovery boiler using external non-contact black liquor evaporation and a dry bottom precipitator. In this system, the flue gas was not passed through the evaporator where it would pick up reduced sulfides (TRS). Problems, mostly mechanical, were encountered with these dry bottom precipitators, and the wet bottom designs had a resurgence. Freyaldenhoven, et al.<sup>2</sup> have cited limited testing which has indicated that malodorous emissions from these wet bottoms (fed with unoxidized 65% black liquor) are negligible.



Corrosion is a serious problem in electrostatic precipitators. The  $\text{SO}_3$  gas produced in the recovery boiler may react with water in the flue gases to form sulfuric acid. The sulfuric acid may then condense on the internals of the electrostatic precipitator if the temperature falls below the acid dewpoint. Hydrochloric acid also can condense on surfaces at lower temperatures or form by reaction between the sulfuric acid and salt. The resulting mixture of acids may cause severe corrosion to the electrostatic precipitator (ESP).

A TAPPI survey<sup>1</sup> of ESP operations has examined corrosion problems. The survey considered 22 areas of corrosion. Their findings are summarized in Table 1. Level 2 corrosion was defined as "noticeable corrosion that may require repair in the future."

Table 1. TAPPI Survey of ESP Corrosion.<sup>1</sup>

Area of Corrosion	Percent of Units with > Level 2 Corrosion
1. Insulator bushing openings	6
2. Around roof access doors	6
3. Around sidewall access doors	71
4. Upper corners at hot roof	7
5. Inside hot roof and on basins	6
6. On top of plates	0
7. Sidewalls at vertical corners	47
8. Sidewalls, general	18
9. Inlet vanes and inlet area	18
10. Outlet vanes and outlet area	53
11. Wire weight guide frames	10
12. Mechanical hammer supports	0
13. Lower edges of collecting plates	0
14. Instrument penetrations	20
15. Dry bottom pan area	31
16. Wet bottom pan area	66
17. Dry drag scrapers	21
18. Dry cross conveyors	60
19. Wet/dry cross conveyors	25
20. Attachments	9
21. Ductwork	64
22. Steel stack	66

The survey identified four 'major' areas of corrosion: sidewalls at vertical corners, outlet vanes and outlet area, ductwork and sidewall access doors.<sup>1,3</sup> 'Limited' areas of corrosion were identified as wire weight guide frames, sidewalls, inlet vanes and inlet area, instrument penetrations, dry drag scrapers/dry bottom pan area, wet/dry cross conveyors, wet bottom pan area, and steel stacks.

## FAILURES/PROBLEM AREAS

## DISCHARGE ELECTRODES AND COLLECTOR PLATES

Discharge Electrode Failures

The steel frames used to support groups of the ionizing electrodes are insulated from ground potential by porcelain, alumina or silica insulators.<sup>4</sup> An example of corrosion in the area of the electrical feedthrough is illustrated in Fig. 1. This corrosion may be attributed to localized cooling due to poor insulation or air in-leakage. Heated purge air (kept to a minimum) should be used to keep the support insulators clean and free of moisture.<sup>5</sup> Corrosion fatigue can occur at discharge electrodes at terminations and high-voltage strap connections.<sup>4</sup>

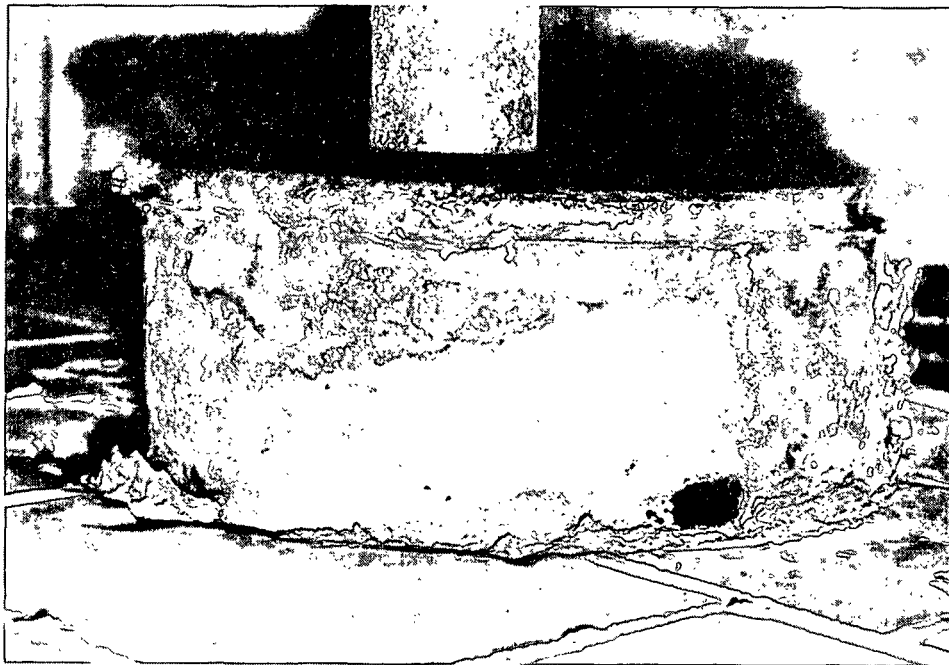


Figure 1. Corrosion at a high-voltage feedthrough.

Collector Plates

One of the areas most vulnerable to corrosion is collector plates. They suffer uniform corrosion, and intergranular attack may occur at supports.

Corrosion fatigue can occur at collecting plate hanger areas. The plates adjacent to the outer shell walls are subject to the maximum temperature variations and may experience temperatures below the dewpoint. The lower portions of the collector plates, especially toward the gas outlet of the precipitator (where the flue gas is cooler), become sensitive to temperature variations.<sup>4</sup> Lyttle and Dawson<sup>6</sup> described severe corrosion of collector plates, especially at the bottoms. Figure 2 illustrates the severe corrosion which may be observed in this area. The top portions of the collector plates can be affected by the flow of air through support insulators.<sup>4</sup> The TAPPI survey<sup>7</sup> found no significant differences between the designs of collectors. Rigid frame and weighted wire types did not experience significant differences in corrosion. The TAPPI survey<sup>1,3</sup> found one respondent had noticeable corrosion at wire weight guide frames. That unit also had very low flue gas temperature, no bottom insulation and had been in service seven years. Units reporting no corrosion had bottom insulation or flue gas temperatures greater than 177°C (350°F) at the collector outlet. Thus, low temperature (especially in 'cold spots') appears to be the major cause of corrosion of collector plates.

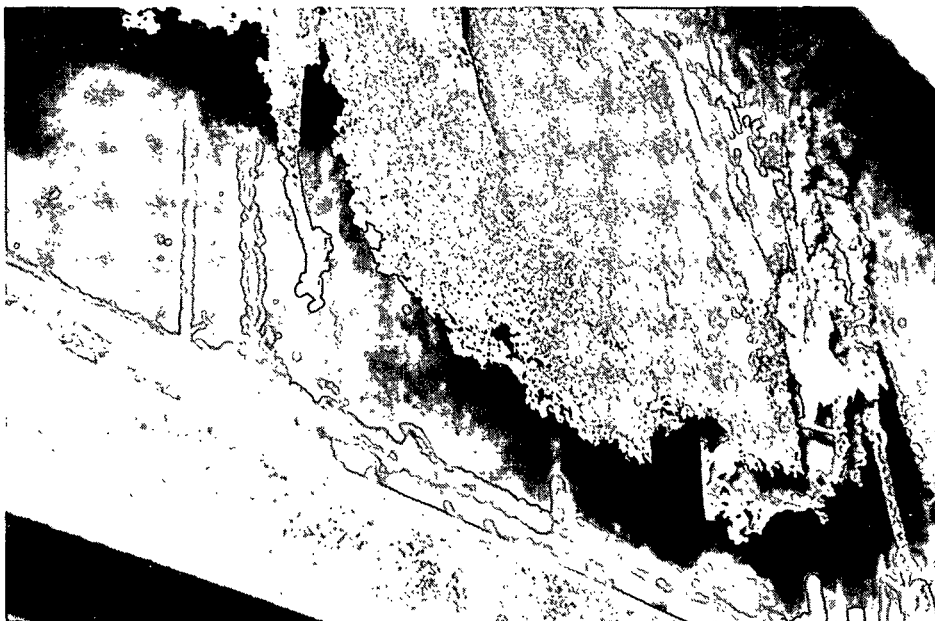


Figure 2. Corrosion at the bottom of a collector plate.

## PRECIPITATOR SHELL

Prior to 1970, most ESP's had reinforced tile outer shells. The tile was either filled with concrete or left hollow. The support structures were steel. Tiles were glazed on one side and webbed on the back. Failure of the webs caused delamination. This failure was due to corrosion of the mortar, excessive heat, spalling, and cracking from expansion and contraction. Figure 3 illustrates the loss of grout in one ESP. Corrosion of the exposed reinforcing steel could then occur as seen in Fig. 4. After 1970, most construction was entirely steel.<sup>8</sup>

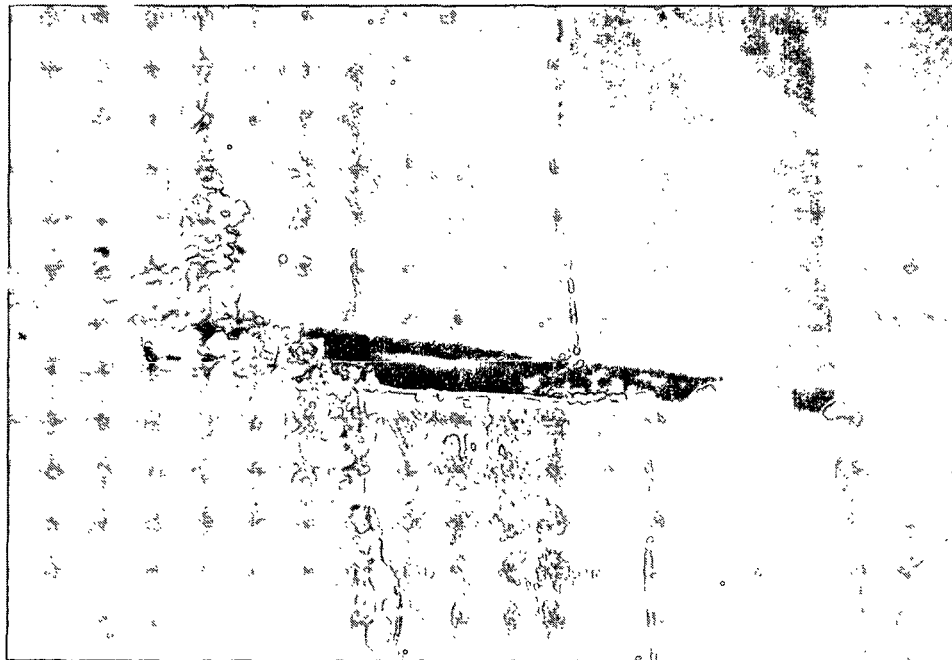


Figure 3. Loss of grout inside of an electrostatic precipitator.

A major area of corrosion of the shell was on the sidewalls at vertical corners. The principal factors in the corrosion were age, sulfidity, heated shell, and precipitator velocity. In the TAPPI survey, five units had heated shells and reported no corrosion. In these five units, the age varied

from 3-7 years, sulfidity varied from 20-28%, and flue gas temperature varied from 175 to 210°C (347 to 411°F). For units without a heated shell, age and sulfidity were the major factors influencing corrosion, but flue gas velocity was a contributing factor. The highest corrosion rates for heated shells occurred at sulfidities above 27% and at an age greater than six years.<sup>1,3</sup> High sulfidity could increase corrosion rate by increasing SO<sub>3</sub> concentrations in the flue gas and consequently sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) concentration.

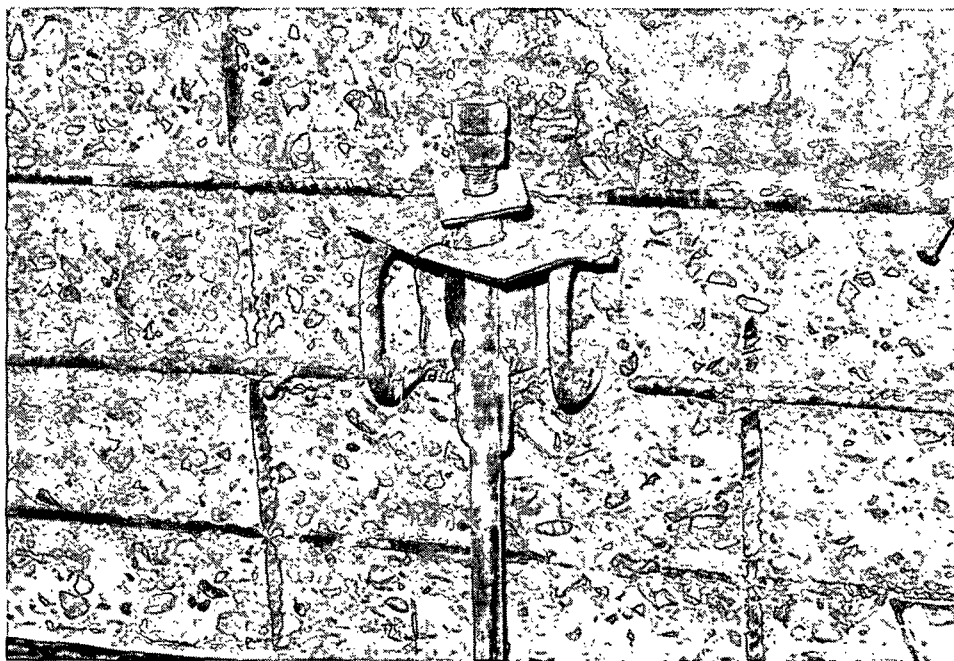


Figure 4. Exposed reinforcing steel.

Side wall access door corrosion was identified as another major area of corrosion. Severe corrosion of an access door is illustrated in Fig. 5. Severe spalling and complete loss of carbon steel in the vicinity of an access door is illustrated in Fig. 6. The damage was more severe near the door due to air in-leakage or poor insulation. According to the survey, access door corrosion was influenced by heated shell, induced draft (ID) fan location (clean or dirty) and age. The units with a heated shell, a dirty ID fan and shorter time in service

generally had less access door corrosion. For units with a clean ID fan and without a heated shell, a double type access door gave longer life.<sup>1</sup> The corrosion was affected by deterioration of seals around doors with time.



Figure 5. Corrosion of an access door.



Figure 6. Concrete damage near an access door. The door is on the left-hand side.

Limited sidewall corrosion was associated with a rigid type bottom support (no slide plate supports) and no heated shell.<sup>1,3</sup> Corrosion of expansion joints is a problem.<sup>4</sup>

Localized corrosion of the structure is often the result of air in-leakage. This occurs at doors, test ports, expansion joints, access doors, damper seals, flue and precipitator connections, and rapper rods.<sup>5</sup> The air lowers the temperature below the dewpoint and provides moisture which raises the local dewpoint. This air leakage can lead to moistening of salt cake.

#### DUCTWORK, INLETS, AND OUTLETS

Ductwork corrosion was identified as a major problem. Ductwork corrosion occurred in areas of salt cake buildup. Buildup may have been due to inadequate flue gas velocities. The major factors influencing corrosion were age, sulfidity, ID fan location, precipitator velocity (as an index of duct velocity) and number of outages per year. Individual operators reported corrosion caused by air in-leakage (around access doors or expansion joints), salt cake build-up, or low load operation.<sup>1,3</sup> Salt cake buildup is indicative of low temperature, low velocity, or localized high dewpoint (perhaps due to air in-leakage).

Although corrosion at outlet areas and outlet vanes was a major problem, no consistent reason for corrosion could be identified.<sup>1</sup> Corrosion at inlet vanes and in the inlet area was associated with low precipitator velocity (0.7 m/s or less).<sup>1</sup> Presumably, hangup of dust and poor circulation were problems.

Stack problems were associated with low flue gas temperatures of 175°C (345°F) and lack of insulation.<sup>1</sup>



## BOTTOM PAN

Dry Bottom Designs

Dry drag scrapers and dry bottom pan area problems were associated with an absence of bottom insulation and use of rigid column supports. The survey identified this as a 'limited' corrosion problem.<sup>1,3</sup> Precipitators with corrosion problems with all dry cross conveyors were at least 6 years old. One facility had a flue gas temperature of 177°C and no bottom insulation. Corrosion also was observed in the feed section or trough above the conveyor or in the transition to the mix tank, not in the conveyor itself. The survey identified this as a limited problem area.<sup>1,3</sup>

Some difficulties were reported in dry-bottom precipitators with backflow from the salt cake mix tank. According to Caron<sup>9</sup> this was confined to those installations where the electrostatic precipitator was equipped with an ID fan. Under conditions of economizer pluggage, an imbalance in flow between the inlet and the outlet of the precipitator resulted in the unit being operated under a higher negative pressure than usual. In turn, this resulted in a reverse flow from the salt cake mix tank that carried moisture up the salt cake discharge trough. This resulted in the clogging of the salt cake discharge and localized corrosion in the bottom of the precipitator.<sup>9</sup>

Wet Bottom Designs

Corrosion of wet bottom pans is generally confined to the liquor/flue gas interface. This results from the flue gas temperatures falling near or below the dewpoint in this area, as liquor temperatures are generally lower than gas temperatures. Figure 7 illustrates corrosion at a baffle plate in a wet bottom precipitator at the liquid/gas interface. According to the TAPPI survey,

problems with the wet bottom pan area were in units without bottom insulation and without a stainless inner side wall.<sup>1,3</sup> A better material may be called for in this area.



Figure 7. Corrosion at the liquid/gas interface of a baffle plate in a wet bottom precipitator.

The joint between the top of the wet bottom pan and the wall is a problem area. Due to thermal differential expansion between the wet bottom pan ( $93^{\circ}\text{C}$ ) and the main precipitator structure ( $191^{\circ}\text{C}$ ) care must be taken to ensure freedom of movement between the two systems. Without this freedom, welded joint cracking can occur with subsequent liquor leakages.<sup>1,2</sup>

An installation that suffered corrosion in wet or dry cross conveyors (including ribbon mixers and sluice troughs, serving a dry bottom) reported outlet flue gas temperatures of  $168$  and  $170^{\circ}\text{C}$  ( $334$  and  $338^{\circ}\text{F}$ ). Other units, with no corrosion, had temperatures above  $193^{\circ}\text{C}$  ( $380^{\circ}\text{F}$ ).<sup>1</sup> Again, the importance of temperature is confirmed.

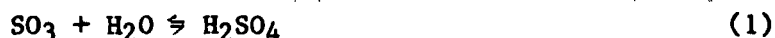
## INSTRUMENT PENETRATIONS

Corrosion at instrument penetrations was generally associated with poor insulation and sealing. The TAPPI survey showed this to be a 'limited' area of corrosion.<sup>1</sup> They identified test ports as another source of trouble.<sup>4</sup> Air in-leakage at the rapper rods, where the elastomeric boots are torn or damaged, is another area where a penetration of the wall can lead to corrosion.<sup>8</sup> Careful inspection and sealing would solve many of these problems.

## MECHANISM

## DEWPOINT

As noted already, corrosion in electrostatic precipitators is caused by sulfuric acid formed from the sulfur trioxide in the flue gases. This occurs via



Thus  $\text{SO}_3$  and  $\text{H}_2\text{O}$  concentration are vital factors in determining dewpoint and therefore corrosion. This sulfuric acid in the flue gases can condense if the temperature falls below the dewpoint for the acid. The Verhoff-Banchero equation can be used to determine the acid dewpoint once the  $\text{SO}_3$  and  $\text{H}_2\text{O}$  compositions are known.<sup>10,11</sup>

$$T_{dp} = \frac{1000}{1.7842 - 0.0269 \log P_{\text{H}_2\text{O}} - 0.1029 \log P_{\text{SO}_3} + 0.0329 \log P_{\text{H}_2\text{O}} \log P_{\text{SO}_3}} \quad (2)$$

where  $T$  is degrees Kelvin and pressures are in atmospheres. Alternatively, the  $\text{SO}_3$  concentration could be estimated if acid dewpoint and water content were known. Dewpoint increases as  $P_{\text{SO}_3}$  and  $P_{\text{H}_2\text{O}}$  increase, which means that in gases with more  $\text{SO}_3$  acid can deposit at higher temperatures. Thus, equipment does not have to be as cool for acid condensation to form on it and corrosion to occur. Under these circumstances, the corrosion may be more widespread, assuming the temperature distribution to remain the same. Alternatively, Eq. (2) may be rewritten in terms of  $P_{\text{H}_2\text{SO}_4}$  instead of  $P_{\text{SO}_3}$ .<sup>5</sup> This relationship is illustrated in Fig. 8.

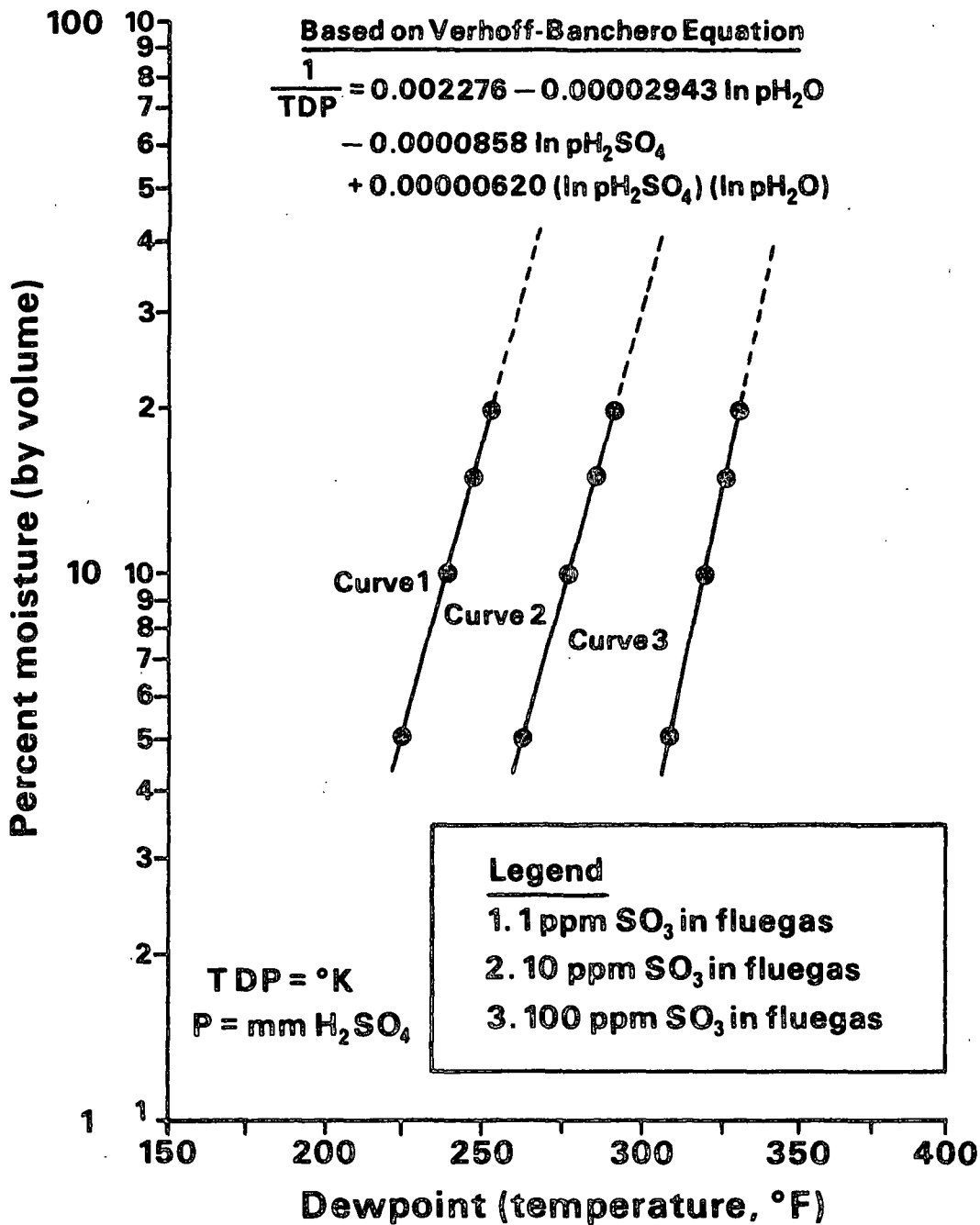


Figure 8. SO<sub>3</sub> dewpoint for varying moisture and SO<sub>3</sub> concentrations in flue gases. Source: Research Cottrell Inc.<sup>5</sup>

McDonald and Dean<sup>12</sup> have reviewed literature on the sulfuric acid dewpoint. The determination of the dewpoint is difficult due to the very low partial pressure of H<sub>2</sub>SO<sub>4</sub>. They presented graphs of dewpoints and condensate composition for vapor mixtures of H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> at 760 mm Hg total pressure

shown in Fig. 9 and of  $\text{H}_2\text{SO}_4$  dewpoints for typical flue gas moisture concentrations, Fig. 10. They pointed out that changes in moisture can have a significant effect on the predicted sulfuric acid dewpoint. If a surface is maintained at a temperature lower than the acid dewpoint but higher than the water dewpoint, the concentration of acid condensate which occurs can be predicted if the water vapor content of the gas is known.

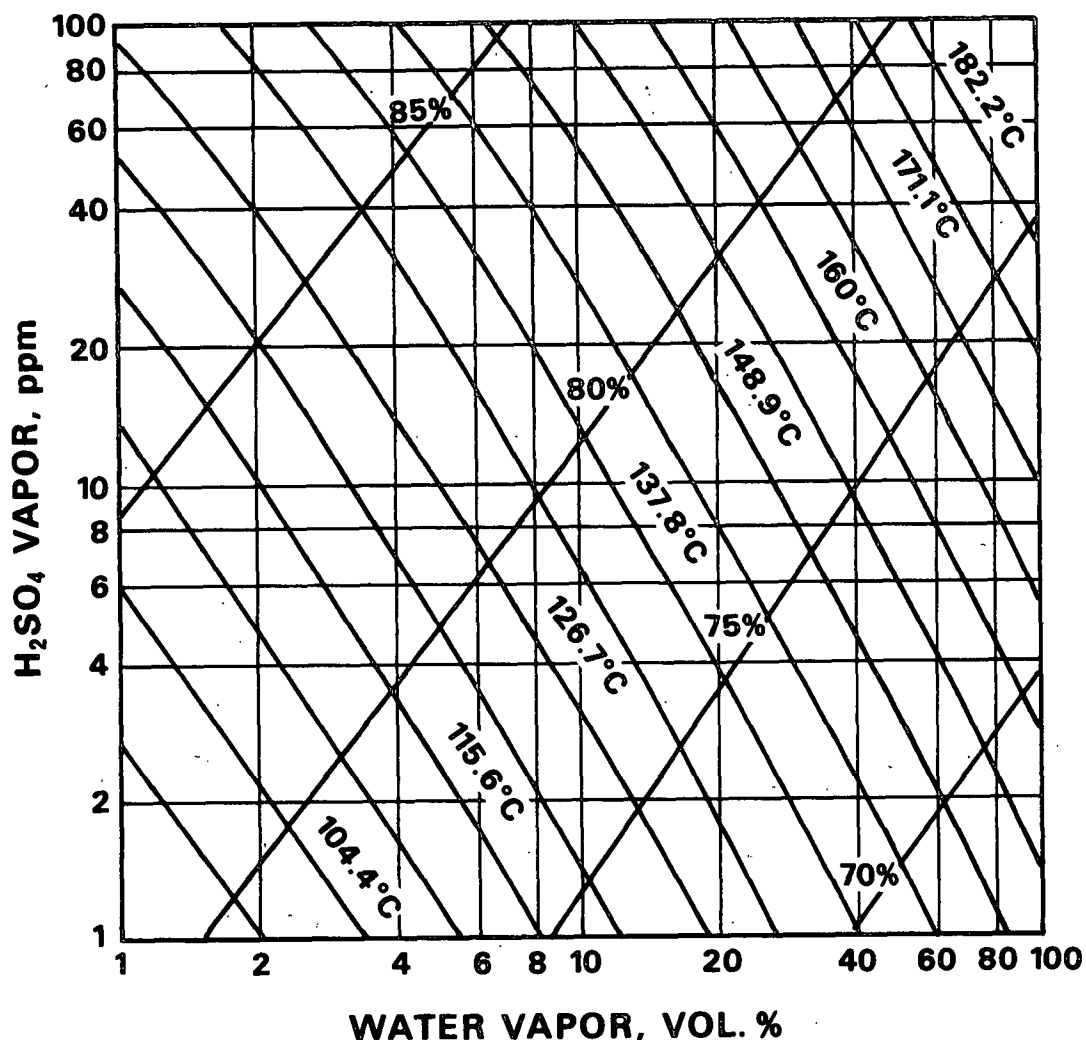


Figure 9. Dewpoint and condensate composition for vapor mixtures of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  at 760 mm Hg total pressure.<sup>12</sup> Reproduced with permission of Noyes Data Corporation.

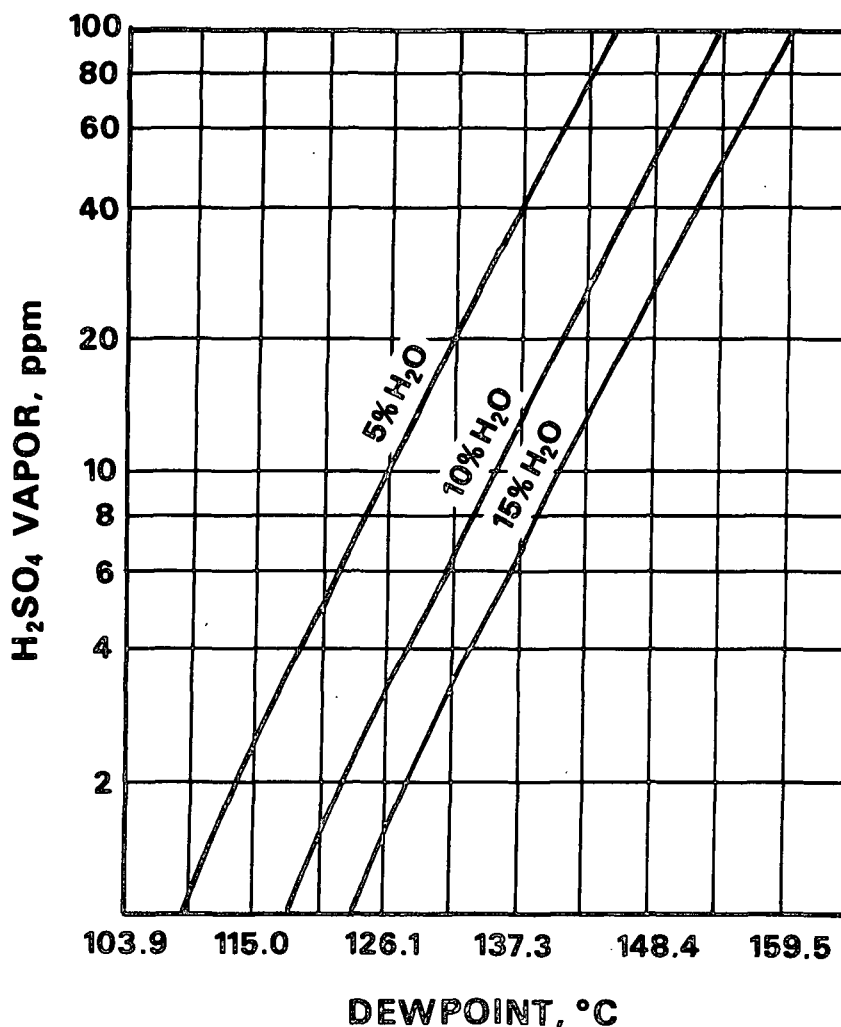


Figure 10. H<sub>2</sub>SO<sub>4</sub> dewpoints for typical flue gas moisture concentrations.<sup>12</sup>  
Reproduced with permission of Noyes Data Corporation.

The SO<sub>3</sub> (or H<sub>2</sub>SO<sub>4</sub>) in the flue gas can affect dewpoint temperatures at a given moisture content. Condensation of moisture and dilute acid in the precipitator can occur due to operating conditions, particularly during startups, shutdowns or low loads. The acid concentration in the condensate will be decreased as the dewpoint is decreased.<sup>13</sup> At the lower temperatures, water is present in the condensate. Thus, as SO<sub>3</sub> increases and dewpoint increases, the moisture increases in the salt cake, making it sticky.

Instrumentation for dewpoint measurement is available as a conductivity probe produced by Land Pyrometers Ltd. A Pt:Pt/Rh thermocouple in a standard glass or ceramic annulus or thimble is cooled internally by air. As the tip cools and condensate forms, a conductive film develops and allows a small current to flow. As more condensation forms, conductivity increases. One drawback to this probe is the difficulty of keeping the thimble clean.<sup>14</sup>

## CORROSION

As described above, corrosion occurs because of the formation of acid. The temperature,  $\text{SO}_3$  concentration, and  $\text{H}_2\text{O}$  concentration are important. The mechanism of corrosion in electrostatic precipitators is poorly defined, especially as it is affected by recovery boiler operation. Almost no information is available on corrosion rates in electrostatic precipitators used in the pulp and paper industry. The presently accepted mechanism involving  $\text{H}_2\text{SO}_4$ , described above, may be affected by unidentified process variables.

Corrosion can be influenced by the amount and concentration of acid formed. McDonald and Dean<sup>12</sup> have published graphs of acid condensate concentration vs. temperature for a range of flue gas water vapor pressures. Using corrosion data by Piper and VanVliet,<sup>15</sup> they showed that corrosion rate increased as  $\text{H}_2\text{SO}_4$  concentration decreased (and temperature increased). According to McDonald and Dean,<sup>12</sup> corrosion is more strongly related to the amount of condensate deposited than to the concentration of the condensate. At dewpoint temperatures common in normal utility precipitator systems, a dilute acid condensate may form which is frequently more corrosive than concentrated acid conditions. They discussed the case of a steel surface at  $126^\circ\text{C}$ . If the flue gas has 10% water vapor and 10 ppm sulfuric acid vapor, the condensate



would be 77%  $\text{H}_2\text{SO}_4$ . If the sulfuric acid vapor is increased to 80 ppm, the condensate strength would remain 77%  $\text{H}_2\text{SO}_4$  but much more condensate would form. Decreasing the temperature would dilute the acid, making it more corrosive. Thus, materials must resist a wide range of acid strengths. On the other hand, Meadowcroft and Cox<sup>16</sup> have reproduced data on corrosion of steel in solutions of  $\text{H}_2\text{SO}_4$ , which show that corrosion rate is much more dependent on temperature than acid concentration. Results for Alloy C276 showed little dependence of corrosion rate on concentration, although rates were much lower than for steel. In bulk solutions of concentrated  $\text{H}_2\text{SO}_4$  (>70%), iron sulfate film protects the surface unless it is damaged by abrasion or fluid velocity.

Flint and Kear<sup>17</sup> found that, irrespective of the dewpoint temperature, the rate of corrosion reaches a maximum at a surface temperature of the steel between 20 and 45°C below the dewpoint as illustrated in Fig. 11. They found that the concentration of condensed acid changed little with surface temperature. The maximum rate of condensation of acid corresponded with the maximum corrosion rate. The maximum corrosion rate does not occur at the dewpoint because apparently there is less acid present at the dewpoint. The corrosion rate is governed by the rate of acid deposition and not by the rate of reaction between metal and acid. The importance of minimizing acid buildup is apparent from this result.

Flint's findings that maximum corrosion rate occurred below the dewpoint, where condensation was maximum, were confirmed by Clark and Childs<sup>18</sup> and by Dawson et al.<sup>19</sup>

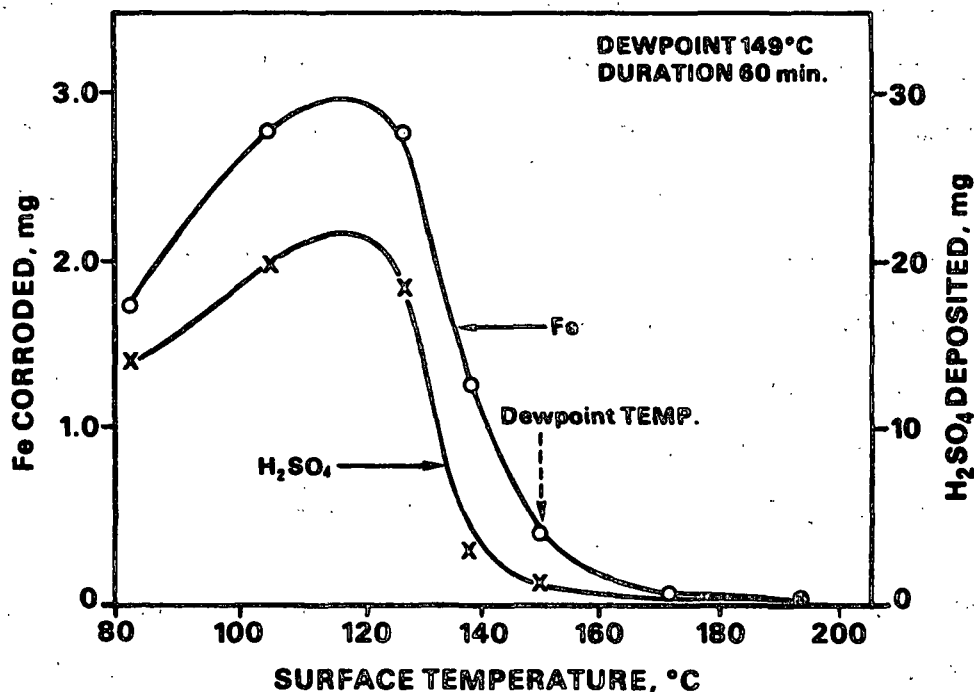


Figure 11. Effect of surface temperature on condensation and corrosion with a dewpoint of 149°C.<sup>17</sup>

Since corrosion rate is related to the rate of acid deposition, acid deposition rate may be measured to determine the point of maximum corrosion rate. Conductivity probes may be used to measure acid deposition rate. The increase in conductivity of the condensate film is monitored at various temperatures, and the rate of acid buildup is estimated from the conductivity changes. In an alternative technique, a lance is inserted into the gas stream. Cooling is applied to vary the temperature along the length. After a time, the lance is removed and condensed acid is collected from sections of the lance.<sup>14</sup>

Hydrochloric acid also forms in the vicinity of the water dewpoint, causing increased corrosion. Hydrochloric acid gas may be present from combustion in the recovery boiler. Deposited H<sub>2</sub>SO<sub>4</sub> may also react with chloride in the salt cake to produce HCl. This chloride arises from logs, water and fuels

used in the process. McDonald and Dean<sup>12</sup> considered HCl formation to be a problem only if temperatures near the water dewpoint were encountered. The HCl itself would be expected to condense in this temperature range. Data by Kear<sup>20</sup> show a great increase in corrosion rate at temperatures below the water dewpoint (40 C). Acceleration of corrosion rate due to HCl below the water dewpoint also was measured by Piper and VanVliet.<sup>15</sup> Thus, chloride may exert a significant influence on corrosion rate, especially at temperatures near the water dewpoint.

The salt cake and the acid itself are hygroscopic and may absorb moisture if cooled. This will lead to formation of a poultice under which corrosion may be intensified. Very little information is available on this effect.

## EFFECT OF OPERATING VARIABLES

## TEMPERATURE

To prevent condensation of acids, the temperature must be maintained above the acid dewpoint. In practice, it is difficult to avoid excursions into the acid dewpoint range. These excursions may result from process upsets, overnight shutdowns, air heater operation, underutilization, faulty insulation or poor sealing. In some cases, condensation of water during off-line periods may be as great a problem as on-line acid condensation.<sup>19</sup> Three main factors affect the flue gas temperature.<sup>1</sup> They are feedwater temperature, economizer cleanliness, and boiler load.<sup>1</sup> Presumably, temperature rises if the economizer is dirty or the feedwater is warmer. Low loads on the boiler would be associated with lower temperatures. It is desirable to maintain the flue gas temperature 28°C (50°F) above the dewpoint to allow for partial load operating conditions and low temperature areas in the precipitator.<sup>5</sup>

Flue gas temperature affects corrosion as shown by a TAPPI survey<sup>7</sup> of noncontact evaporator ESP's, which found that those units with no corrosion averaged a test temperature of 196°C (384°F) and those with a serious problem averaged a test temperature of 183°C (361°F). The survey found that although flue gas temperature did not correlate very well with corrosion, if the units were grouped by age, sulfidity, and shell arrangement, a weak correlation with flue gas temperature was seen.<sup>3</sup> One would expect greater corrosion rate as temperature decreases closer to the H<sub>2</sub>SO<sub>4</sub> dewpoint, but the results indicate that other factors must enter into the effect. Operation may be one of these factors. Furthermore, 'average' test temperatures can hide a multitude of variations. Gas composition is one very important factor in determining what affect flue gas temperature will have.

Low temperature areas may be localized within an ESP. In dry bottom precipitators, lack of insulation, higher moisture and slower gas velocities probably result in a much colder bottom pan area with sticky salt cake.<sup>1</sup> Furthermore, some operators have reported that temperature variations occur within the precipitator (especially from top to bottom), and such variations could influence "cold spot" formation and thus corrosion.<sup>1</sup> The TAPPI survey<sup>1</sup> reported a study by Wheelabrator-Frye which showed that significantly lower temperatures occurred in the bottom area. Without the heated shell in operation, the bottom sidewall temperature was 28°C (50°F) lower than the inlet gas temperature. This lowered temperature may have placed it in jeopardy.

Flue gas distribution may have a large effect on local temperatures. For example, Lyttle and Dawson<sup>6</sup> reported severe corrosion of a precipitator due to operation in the same temperature range as the stack gas dewpoint. They measured temperature profiles across the inlet ducts, outlet ducts and in the inlet plenum just as the flue gas leaves the collecting plate area. There was an average temperature drop across the precipitator of 17°C (32°F) caused by natural heat loss, tramp air leaks and some evaporation of black liquor in the wet bottom. Temperature profiles in the outlet plenum showed that they had a flue gas distribution problem. The flue gas was colder across the bottom, across the top in the corners, and against the top and bottom of the division wall which separated one side of the precipitator from the other. Similarly, Caron<sup>21</sup> reported that one of the main difficulties with ESP's was the inlet gas flow distribution. These difficulties may lead to local areas in which temperature falls below the acid dewpoint. Poor distribution and local areas of low temperature will compound difficulties with low temperature resulting from upset conditions or operating difficulties. Thus these effects may be intensified in a poorly operated ESP.

## FLUE GAS COMPOSITION

Sulfur Trioxide

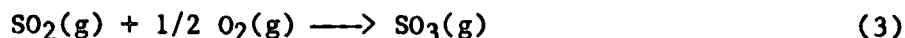
Flue gas composition affects dewpoint as described via the Verhoff-Banchero relation, Eq. (1) and Fig. 11, and confirmed by measurements of dewpoint made by Lisle and Sensenbaugh.<sup>22</sup> Both  $\text{SO}_3$  and  $\text{H}_2\text{O}$  contents influence dewpoint (and thus corrosion rate). The  $\text{SO}_3$  composition is affected by furnace firing temperature, fuel-air ratio, primary-secondary air ratios, and furnace bed temperature and configuration.<sup>5</sup> A high level of excess air increases heat losses and favors formation of  $\text{SO}_3$  and sulfuric acid that, in part, decrease the pH and smelting point. This makes the dust particles sticky.<sup>23</sup> This stickiness may also be partly due to water absorbed by the acid formed. (The acid is hygroscopic.)

Early nondirect contact evaporator type kraft recovery furnaces with direct contact of the heated incoming air with the black liquor as the final stage of liquor concentration, initially operated at exit gas temperatures of  $177^\circ\text{C}$  ( $350^\circ\text{F}$ ) and  $\text{SO}_2$  concentrations in excess of 1000 ppm in the flue gas. This practice resulted in the generation of an extremely sticky particulate of low pH that adhered to all surfaces and resulted in cases of excessive corrosion on some air heaters and precipitators.<sup>9,21,24</sup> Most of the electrostatic precipitators currently operated on NCE kraft recovery furnaces perform at a temperature of about  $204^\circ\text{C}$  ( $400^\circ\text{F}$ ) and a stack gas that normally has less than 300 ppm of  $\text{SO}_2$ . Under these conditions, condensation does not pose a corrosion threat and a sticky salt cake would not be expected.<sup>9,21</sup>

The  $\text{SO}_2$  and  $\text{SO}_3$  content of the flue gas is related to sulfidity of liquor being fired.<sup>1</sup> The  $\text{SO}_2$  and  $\text{SO}_3$  levels are greater if the sulfidity is

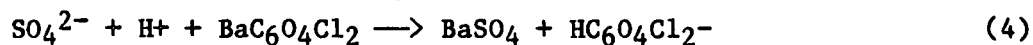
higher. Some  $\text{SO}_3$  is beneficial, and in some power boilers  $\text{SO}_3$  is added to reduce the electrical resistivity of the flyash, improving electrical conditions and ESP performance.<sup>12</sup>

The  $\text{SO}_3$  may be formed by reaction of  $\text{SO}_2$  with oxygen via



This reaction is favored at temperatures below  $537^\circ\text{C}$  ( $1000^\circ\text{F}$ ) with 3% oxygen. However, the kinetics are slow in the absence of a catalyst, so  $\text{SO}_3$  concentration is kinetically limited. At temperatures below  $204^\circ\text{C}$  ( $400^\circ\text{F}$ ), essentially all of the  $\text{SO}_3$  is converted to  $\text{H}_2\text{SO}_4$  by reaction with  $\text{H}_2\text{O}$ .<sup>12</sup>

Understanding of the effect of  $\text{SO}_3$  concentrations is impeded by lack of reliable instrumentation. Besides improving corrosion conditions, chemical analysis and monitoring of exhaust gases would be valuable aids to boiler control, since a minimum sulfur dioxide content indicates improved efficiency and a minimum of excess air. Savings in heat may be achieved if lower flue gas temperatures can be achieved. Sulfur trioxide level may be determined by an acid dewpoint monitor by measuring the dewpoint temperature and relating it to the expected  $\text{SO}_3$  concentration at that dewpoint temperature. Alternatively, the  $\text{SO}_3$  analysis may also be obtained by a colorimetric method.<sup>19</sup> Commercially available equipment for  $\text{SO}_3$  analysis is available from Severn Sciences Ltd. In the monitor, an aqueous isopropanol mixture is used to absorb  $\text{SO}_3$  and prevent oxidation of  $\text{SO}_2$ . The isopropanol mixture is reacted with barium chloroanilate via



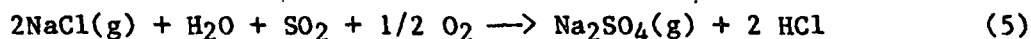
The acid chloroanilate ions released will absorb light of wavelength 535 nm, and

their concentration is measured using a continuous flow photometer. The instrument requires attention at least daily by qualified staff.<sup>14</sup> Instrumented ESP's could allow operation at lower flue gas temperature, achieving substantial heat savings. In conjunction with corrosion rate measurements, the effect of SO<sub>3</sub> concentration on corrosion may be determined and then controlled at an acceptable level.

### Hydrochloric Acid

Hydrochloric acid condensation is expected at a lower temperature than sulfuric acid condensation, and so 'acid dewpoint' usually refers to H<sub>2</sub>SO<sub>4</sub> only. The HCl would condense out between the H<sub>2</sub>SO<sub>4</sub> dewpoint and the water dewpoint. Thus, if temperature is reduced sufficiently below the dewpoint, corrosion can be intensified by HCl formation.

The chloride compounds present in the boiler are the source of chloride for HCl formation. Halstead and Raask<sup>25</sup> found, in pulverized-coal-fired boilers, that all NaCl present in the coal will be vaporized in the combustion chamber. Some of the NaCl will react with SO<sub>2</sub> and water via



The Na<sub>2</sub>SO<sub>4</sub> will condense from the flue gas if the gas is at chemical equilibrium at 927-1127°C (1700-2060°F). They found, experimentally, that NaCl was converted entirely to Na<sub>2</sub>SO<sub>4</sub>. In one plant study, NaCl condensed at 547°C (1016°F). They attributed this to combustion at <2% excess oxygen, or to insufficient time in the burner to convert NaCl to Na<sub>2</sub>SO<sub>4</sub>. The HCl gas produced by reaction 5 may condense at lower temperatures, but if insufficient oxygen is present NaCl would be found at lower temperature in deposits. The effects in recovery boilers may be greater.



In coal-fired power stations, HCl concentration in the flue gas is directly proportional to the chlorine content of the coal. For 0.49-0.56% Cl fuel, HCl concentrations were between 350 and 465 ppm.<sup>26</sup> Similar numbers for recovery boilers are not available. There is little information available on measured concentrations of HCl in flue gases and the effect of it on corrosion.

It is unknown what concentrations of HCl could be expected to form, but some efforts have been made to measure it. Piper and VanVliet<sup>15</sup> claimed that concentrations of HCl in the liquid phase containing H<sub>2</sub>SO<sub>4</sub> are lower than systems containing only HCl and water for a given temperature and partial pressure of HCl. The maximum concentration of HCl expected in a typical stack gas would be much less than 13%. They were unable to predict the maximum temperature at which HCl would be expected in the condensate, but in tests with a condenser, the first chloride was detected at 60°C (140°F). The amount collected increased markedly at lower temperatures. At 45°C (113°F), the concentration of HCl and H<sub>2</sub>SO<sub>4</sub> was between 20 and 30%.

Kear<sup>20</sup> found that above the acid dewpoint temperature the addition of HCl gas did not appear to increase corrosion. Only insignificant amounts of HCl gas can dissolve in or condense with a sulfuric acid film at this concentration (60-80%) and temperature (>150°C). Between the water and acid dewpoints, addition of HCl gas (0.015%) increased corrosion by some 40%. Below the water dewpoint temperature (40°C) a very large increase in corrosion was found and this was greatly accelerated by the addition of hydrochloric acid gas and chlorine. Often chloride is not detected in deposits;<sup>20,26</sup> perhaps the temperatures are too high to permit condensation to occur. Thus, it is only in areas well below the acid dewpoint temperature that HCl would be a problem.

Moisture, TRS, and Dust

Venting dissolving tank vent gases into the precipitator has been identified as a bad practice because it introduces moisture to the precipitator.<sup>1</sup> This moisture can react with  $\text{SO}_3$  to form the  $\text{H}_2\text{SO}_4$ . Caron<sup>9</sup> noted that this cool moist gas stream may channel and encourage the sticking of dust. Moisture also can be introduced by lancing or 'soot-blowing'. In this practice, steam is used to remove ash from the economizer.

The effect of TRS on corrosion rates has not been described in the literature, although it would be expected to have a negative effect just as reduced sulfides (e.g.,  $\text{H}_2\text{S}$ ) stimulate atmospheric corrosion.

Medium to high concentrations of fine particles in the gas stream can sometimes further raise effective dewpoint, according to Hall and Katz.<sup>4</sup> Thus high dust concentrations present during periods of instability, or sootblowing may increase the chance of acid deposition.

SALT CAKE COMPOSITION

Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is the main constituent of salt cake which is carried into the precipitator. As an example, analysis of a sample of recovery boiler precipitator dust at IPC showed that the dust contained 97%  $\text{Na}_2\text{SO}_4$ , 1.7%  $\text{NaCl}$ , 0.25%  $\text{Na}_2\text{CO}_3$ , 0.03%  $\text{Na}_2\text{S}_2\text{O}_3$  and various metals. It is not known whether this is typical. Presumably, the physical properties of the flyash will depend on its composition.

Hydrated sodium sulfate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , has a melting point of  $32.4^\circ\text{C}$  ( $90.5^\circ\text{F}$ ) and should lose its hydrated water at about  $100^\circ\text{C}$  ( $212^\circ\text{F}$ ). This may account for its stickiness at low temperature. Acidic 'sticky' salt cake caused

by high  $\text{SO}_2$ - $\text{SO}_3$  emissions has resulted in significant air heater and precipitator problems as described previously.

Salt cake is hygroscopic but this should not affect the dewpoint. The ESP Handbook<sup>12</sup> states that, although fly ash particles can influence the apparent dewpoint, or saturation temperature of  $\text{H}_2\text{SO}_4$  in flue gas, experience has shown no errors in neglecting other gases and considering only the system sulfuric acid/water. This is in contrast to Hall and Katz,<sup>4</sup> who thought that high concentrations of fine particles could raise effective dewpoint. This matter needs further investigation.

There is evidence that the salt cake is not very corrosive, but is simply a medium for corrosive acids, etc. Rabald<sup>27</sup> has listed steel as being resistant to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  at room temperature to boiling point, with corrosion rates less than  $1 \text{ g/m}^2$  per day. It was also fairly resistant to corrosion (up to  $24 \text{ g/m}^2/\text{day}$ ) at  $250$ - $300^\circ\text{C}$ .

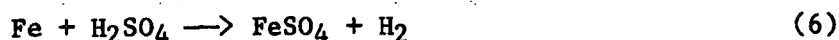
In tests with a condenser in a stack, Piper and VanVliet<sup>15</sup> observed that deposits were dry in appearance above  $66^\circ\text{C}$  ( $150^\circ\text{F}$ ). As the temperature was reduced, they became more sticky and moist. At  $41^\circ\text{C}$  ( $105^\circ\text{F}$ ), the deposit consisted of nearly equal parts of solid and liquid and was sufficiently liquid to flow. It is reasonable to assume that this will provide a medium in which corrosion may occur. It also seems reasonable that the moisture absorbed by the salt cake could increase the volume of acid formed and thus the corrosion rate.

High chlorides and low pH will tend to promote crevice attack under scale deposits, as well as pitting.<sup>11</sup> This may be the case with salt cake deposits, but there is no published evidence to support this. Heavy corrosion

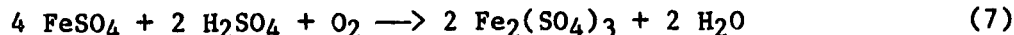
near deposits may be due to acid formation which caused the build-up of salt cake, but may only be coincidental with the salt cake.

One factor which has not been examined is the influence of oxidized sulfur species in the salt cake. These may include thiosulfate,  $(\text{Na}_2\text{S}_2\text{O}_3)$ , which has been shown to increase the possibility of corrosion in white liquors.<sup>28</sup> The effects under salt cake or in wet bottoms of precipitators is unknown.

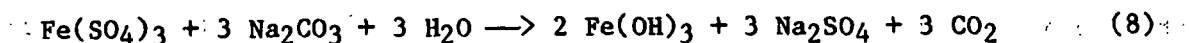
Corrosion deposits may be incorporated into the salt cake and this may be especially important at the metal surface. McDonald and Dean<sup>12</sup> have noted that during corrosion, ferrous sulfate forms via



then reacts further to ferric sulfate via



This may react with soda ash  $\text{Na}_2\text{CO}_3$  via



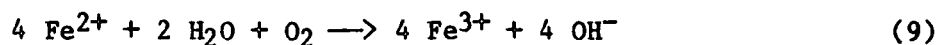
The  $\text{Fe}(\text{OH})_3$  (ferric hydroxide) is undesirable because it is a sticky gelatinous compound difficult to remove. McDonald and Dean<sup>12</sup> performed corrosion tests which indicated that basic flyash neutralized a major portion of the acid as it condensed but that this effect was limited to a surface layer. A layer of  $\text{CaSO}_4$  then formed and prevented the underlying soluble base from being utilized.

The role of  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  in the corrosion has been studied by Dawson et al.<sup>19</sup> They found that, unlike tests carried out in bulk acids, the passivation by  $\text{FeSO}_4$  was not maintained under thin film conditions. The corrosion rate

increased after 5-12 h, and visual examination suggested that the sulfuric acid was becoming diluted due to water absorption. They noted that  $\text{FeSO}_4$  may be hydrated with 1, 4, or 7  $\text{H}_2\text{O}$ , depending on the humidity. When the water vapor pressure exceeds the standard vapor pressure of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , the salt will form a solution in equilibrium with the water vapor pressure. In tests with  $\text{FeSO}_4$  crystals, passivation was accompanied by drying out of the surface, followed by hygroscopic absorption of water and flooding of the surface. They noted that this phenomenon was similar to the sweating which is observed in plants after shutdown. Corrosion problems in electrostatic precipitators are compounded because the acid, the salt cake and even the corrosion product are hygroscopic.

#### AIR INGRESS

Air in-leakage lowers the temperature below the dewpoint, increasing the rate of acid deposition. Also, it may locally reduce the moisture content of the flue gas, reducing the dewpoint temperature and raising the acid concentration. Oxygen may also raise the dewpoint by increasing the  $\text{SO}_3$  concentration, although there is already some  $\text{O}_2$  present in the flue gas. At the lower temperatures, salt cake accumulates as a sticky deposit and forms a poultice which may remain moist for long periods, causing corrosion damage. Oxygen reduction would predominate as the cathodic process, and ferrous oxides and hydroxides would form. As described in Ref. 26, oxygen may also generate  $\text{Fe}^{3+}$  ions by



This ferric ion may increase corrosion rate via



It has been noted previously that ferric hydroxide is a sticky compound which may contribute to buildups.

#### VELOCITY

Typical air velocities for high efficiency precipitators should be of the order of 1 m/s.<sup>1</sup> Above 1 m/s, carryover or 'snowing' can result; that is, ash is carried out of the ESP and 'snows' on adjacent equipment. If the velocity is less than 0.7 m/s, corrosion can be a problem.<sup>1</sup> Volume oversizing can lead to low gas velocities leading to dust buildup on the turning vanes and excessive buildup in the inlet nozzle. The buildups correlate with corrosion problems.<sup>1</sup> In ducts, higher velocities are required to prevent fallout. Serious fallout (dust accumulation) can be experienced at 12 m/s; a design velocity of 18 m/s may be required to prevent fallout.<sup>1</sup> Low velocity may also contribute to formation of cold spots within the precipitator.

#### CLEANING PROCEDURES

Sootblowing is a process for the removal of deposits from the boiler by air or steam jets. This introduces moisture which increases the corrosion rate by increasing the acid dewpoint and by being absorbed into hygroscopic deposits. Dry air sootblowing would be preferable.

If washing of the ESP must be done, it must be done very thoroughly. Following cleaning, the inside must be immediately dried out with gas or oil fire.<sup>5</sup>

## STARTUP AND SHUTDOWN PRACTICES

According to the TAPPI survey, the number of outages per year was a factor influencing corrosion in ductwork.<sup>1,3</sup> The effect may arise because of the cooling down and operating periods at less than full boiler load where temperatures and flows are below design. It would appear to be advantageous to maintain critical areas a few degrees above ambient to prevent moisture pickup during shutdowns. Temperature cycling may cause acidic deposits to absorb moisture as they cool because they are strongly hygroscopic. They become moist and "sweat."

## BOILER OPERATION

The main influence of additions to the black liquor before burning and oil burning in the recovery boiler may be to introduce species which increase the corrosion rate. Additionally, the presence of metals such as vanadium may catalyze  $H_2SO_4$  formation.<sup>13</sup>

## REMEDIES

By describing failure areas or by identifying process variables causing a problem, solutions sometimes suggest themselves. The previous sections of this report have probably suggested some solutions to the reader. This section lists some of the alternative solutions for ESP corrosion which are available and how these might be implemented. More information is needed in many cases and indeed some of the suggestions may be debated. Further research could identify more alternatives, determine the efficacy of these alternatives and provide guidance on implementing changes.

## MAINTAIN TEMPERATURE ABOVE DEWPOINT

1. Flue gas temperature may be increased by removal of tubes from the cascade evaporator or installation of a bypass duct around the cascade evaporator. Usually a flow control device is used to regulate the amount of bypass and thus the temperature of the flue gas.<sup>5</sup> This change would raise temperatures above the dewpoint, thus decreasing corrosion. A penalty would be paid in the loss of heat.

2. Cold spots in the precipitator may be eliminated by improving flow distribution. Areas where air in-leakage is occurring should be eliminated. These areas may be identified by inspection. Monitoring of temperature could be performed to detect excursions of temperature which are common even under steady-state operating conditions.<sup>19</sup> These solutions would demand careful inspection, monitoring and remedial action.

3. Heat jacketing could be installed to make the precipitator double-walled. Heated air is circulated through the heat jacket to eliminate internal



shell cold spots. This would allow for maximum heat recovery from the boiler exhaust gases and thus higher boiler efficiencies. The design should include dampers to adjust the gas flow distribution of heated air. Problems with these systems are often the result of improper system operation and maintenance and high heat consumption.

4. Insulate any area in contact with flue gas or heavy black liquor, especially at the gas/liquor interface.<sup>3</sup> This should include inspection of existing insulation to identify deficiencies.

#### MONITOR AND ADJUST RECOVERY BOILER OPERATIONS

1. Levels of  $\text{SO}_3$  in the flue gas may be reduced by adjusting the boiler firing techniques, e.g., less excess air. Temperature may be increased by changing water flows and boiler load. These changes would be difficult to implement at present because optimum operating conditions have not been identified and, indeed, may vary from system to system.

A computer system may be used to control the operation. For example, Esso Engineering (Europe)<sup>29</sup> has devised a system for minimizing flue gas outlet temperatures. They determined the acid dewpoint temperature in the flue gas system as a function of operating parameters including excess air levels. They then modeled the data to determine acid dewpoint temperature as a function of operating parameters and programmed a process computer to calculate acid dewpoint as a function of operating parameters to minimize flue gas temperature.

Operations of recovery boilers should be monitored in conjunction with measurements of  $\text{SO}_3$  concentration or dewpoint to better characterize the effect of operating parameters.

2. Maximum possible rated flow velocities should be used. Design flue gas temperatures should be reviewed or adjusted upward to minimize the actual low load operating flue gas temperature.<sup>1</sup> If planning to operate at low load for an extended period, velocities should be reviewed to determine their effects.<sup>3</sup> This may be time consuming, but if applied to specific problem areas, it may pay off.

#### PROCESS CHANGES

1. Lower the sulfidity of the liquor to reduce the SO<sub>3</sub> levels.
2. Minimize chloride concentrations.

These changes may be unacceptable (or unattainable), but should be kept in mind when considering changes in process.

#### PERIODIC INSPECTION

1. Identify areas of poor sealing or intense attack and take remedial action. This has been discussed previously.
2. Thorough failure analysis of failed components should lead to improved performance, provided that corrective action is taken.

#### UTILIZE ALTERNATIVE MATERIALS

Some of the alternative materials are described below with information available on their performance. Very little information is available on corrosion rates in pulp mill ESP's.

Carbon and Low-Alloy Steel

Carbon steel is appropriate for use in ESP's where the dewpoint is high enough, even if chlorides are present. If the temperature falls too low, corrosion will accelerate dramatically. For example, Piper and VanVliet<sup>15</sup> found that in stack gases, low-alloy steels corroded 50-75 times more rapidly at 31°C (87°F) than at 61°C (141°F). They noted that Corten steel performed very well. Lyttle and Dawson<sup>6</sup> reported results of weight loss tests in a pulp mill ESP at about 150°C. These results, summarized in Table 2, show a comparison of mild steel with a variety of other materials in a temperature regime near the dewpoint. The corrosion rate on the mild steel is much higher.

Table 2. Corrosion coupon results.<sup>6</sup>

Metal	% of Loss of Weight per Year
Mild steel	33
Lead	1
317L	1
Alloy 400	8
Monel 400	5
Monel 601	2.5
Alloy 825	1.5
Incoloy 825	2.0
904L	0.4
2RK65	0.1

Meadowcroft and Cox<sup>16</sup> have obtained results showing that corrosion rates of low alloy steels were somewhat lower than mild steel (120°C, 1000 ppm SO<sub>2</sub>, 15 ppm SO<sub>3</sub>, 1.3% excess O<sub>2</sub>). They suggested that low alloy steels formed a protective oxide and that the corrosion rate decreased after a few hours of exposure because of formation of a ferrous sulfate surface deposit.

Jansen and Eenholt<sup>30</sup> have quoted a report by Barkley<sup>31</sup> which showed Corten weathering steel to be more corrosion resistant in regenerative air preheaters than carbon steel, cast iron or 316 stainless steel.

### Stainless Steel

Stainless steel is used on pan sides of wet bottom precipitators to reduce high corrosion rates at the liquor gas interface.<sup>1</sup> Stainless steel is generally not necessary on the bottom.<sup>32</sup> Type 304 or 304L stainless steel is used for black liquor connections such as normal and high level overflows. The pan drain connection is normally carbon steel.<sup>1</sup> Stainless steel 304L is used for agitators to give improved erosion protection.<sup>1</sup> Black liquor connections such as normal and high level overflows are 304 SS. Type 304L steel is recommended for agitators.<sup>2</sup>

In gases, the stainless steel may offer no advantage. Piper and VanVliet<sup>15</sup> found that between 46 and 71°C (115 and 161°F), low alloy steels corroded less than 430, 302 and 316 stainless steels. At the water dewpoint, the stainless steel thins more slowly but pits much more rapidly. Lyttle and Dawson<sup>6</sup> found that 304 and 316 stainless steels did not stand up well. Their lab results showed they were attacked by chlorides as well as H<sub>2</sub>SO<sub>4</sub>. It is disquieting to note that they observed attack at the air/liquor interface.

According to Meadowcroft and Cox,<sup>16</sup> only the high Ni/Mo alloys have been found immune to rapid attack. Corrosion rates of nickel alloy 625 and alloy B2 were lower than that of mild steel and comparable to the corrosion rates of these alloys in bulk acid. Similarly, Agarwal, Hodge and Storey<sup>33</sup> found that Hastelloy alloy C-276 was effective in combating dewpoint corrosion in flue gas scrubbers.

### Lead

Lyttle and Dawson<sup>6</sup> suggested that lead was the only coating which could be found that was passive to hot sulfuric acid and was also able to conduct

electricity. However, it would not adhere directly to steel and required a tin underlayer. Piper and VanVliet<sup>15</sup> found sprayed-on lead to be ineffective for protecting low-temperature elements in stack gas. More recently, Brandsema<sup>34</sup> has outlined improved fabrication methods for use of lead in electrostatic precipitators. Perhaps these could be applied more widely.

### Organic Coatings

In the repair of tiled walls high temperature epoxies may be applied over shotcrete repairs to protect them before and after they have cracked due to expansion. The surface is brush-blasted and the epoxy is then rolled on to 60-80 mil thickness. More permanent repairs may be done by bonding on fire brick with a high temperature resistant epoxy bonder. Smaller areas may be filled with a high temperature epoxy mortar mix with a sand/aggregate filler. Vinyl ester coatings may also be applied around areas of air in-leakage.<sup>8</sup>

Piper and VanVliet<sup>15</sup> tried a number of coatings for protection from stack gas including bituminous coatings, epoxy thiokol, epoxy rubber and baked epoxy enamel, neoprene, silicones and silicone alkyds of various formulations and bakings both unfilled and filled with graphite, aluminum and mica, and also many proprietary lacquers. A thiokol vinyl and a graphite-filled silicone furnished fair protection to 100°C (210°F) but failed at higher temperatures.

In tests of plastics for coating heat exchangers, specimens were exposed where 85% H<sub>2</sub>SO<sub>4</sub> condensed onto the tubes at about 104°C (220°F). Best protection was provided by sprayed coatings of a polyphenylene sulfide and a perfluoroalkoxy. Both a fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE) were also as good as the perfluoroalkoxy, except that the former had a lower temperature limit, and the latter was difficult to apply

as a pore-free coating. A polyester thermoset and polyvinylidene fluoride (PVDF) did not possess adequate corrosion resistance, and showed thermal degradation.<sup>35</sup>

Cox et al.<sup>36</sup> found that in laboratory tests in flue gas environments, a fluoroelastomer copolymer showed the greatest resistance in the acid dewpoint range (100-135°C). An isocyanate-cured pitch epoxy and a polyester showed promise. They suggested that loading with suitably oriented inert fillers such as glass flakes should improve performance. These coatings were superior to PVDF, PTFE loaded polyamides, and chlororubbers.

In other tests in flue gas desulfurizer environments, White and Leidheiser<sup>37</sup> found that vinyl ester, fluoropolymer and some epoxies performed well in H<sub>2</sub>SO<sub>4</sub> solutions but that polyester was attacked.

#### Composite Materials

Piper and VanVliet<sup>15</sup> tested FRP in stack gases and found it to remain in fair condition. The surface of the resin had been destroyed on many samples, however, exposing the glass fibers. FRP was considered acceptable for use up to at least 71°C (160°F) but below 149°C (300°F). Later investigations showed FRP to be very acceptable in service at 165°C (330°F) in ducting to and from an ESP.<sup>38</sup> More recently, FRP duct constructed of Atlac 711-05A, a fire-retardant, corrosion resistant resin produced by ICI Americas was operated to 160°C (320°F) without rebuilding the duct system or exhaust stack.<sup>39</sup>

Elastomeric expansion joints constructed of Viton<sup>a</sup> fluoroelastomer in combination with wire mesh, Kevlar<sup>a</sup>, Nomex<sup>a</sup> and Teflon<sup>a</sup> resin have been found to resist operating temperatures up to 204°C (400°F) in flue gas stack systems.<sup>40</sup>

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a = Registered trademark of Du Pont.

### Inorganic Coatings

Piper and VanVliet<sup>15</sup> tested various inorganic coatings. Nickel-phosphorus, fired under reducing conditions, was the best coating, followed by crack-free chrome plate, nickel-phosphorus applied by a wet reduction process and sprayed aluminum. Specimens coated with nickel-phosphorus and crack-free chrome were protected completely at 71 and 60°C (161 and 141°F). At 46°C (115°F), the nickel-phosphorus applied by the wet process corroded through. All coatings were damaged at 31°C (87°F) except the nickel-phosphorus reduced by firing. Sprayed-on aluminum coatings on Corten steel for low temperature elements in stack gas were found to be more resistant than aluminum itself. Aluminum oxide coating exhibited poor adherence. Vitreous enamels provided good protection above 46°C (115°F). They were very resistant but were slightly attacked at 31°C (87°F). The most resistant of the vitreous enamels furnished the best protection for the steel at temperatures below the water dewpoint, of any materials tested.<sup>15</sup>

Cox et al.<sup>36</sup> found that arc-sprayed aluminum, an experimental TiO<sub>2</sub> coating and enamels were resistant to flue gas (to 135°C), but flame sprayed oxide coatings were unsatisfactory.

The area of inorganic coatings requires additional research to identify acceptable coatings for specific applications.

### STRUCTURAL DESIGN

1. In some wet bottom precipitator designs, belly bands (0.5-inch) are used at the liquor/gas interface to compensate for high corrosion rates.<sup>1,2</sup> The use of more corrosion resistant materials for the pan sides may also be considered.

2. Some steel shell collectors designed in the early 1970's were without a side plate bearing system for thermal expansion. The bottom was not insulated. The columns for the precipitator were continuous with the support steel. Based on operator observations, this rigid column system without bottom insulation contributed to bottom pan and sidewall at corner corrosion. The "floating" slide plate system with bottom insulation had fewer corrosion problems.<sup>3</sup>

3. Install double access doors to minimize localized cooling and air in-leakage.

4. Prevent dust hangup on horizontal surfaces by minimizing horizontal areas.

5. Minimize locations where air may leak into the precipitator.



## CORROSION TESTING

According to the TAPPI survey,<sup>1</sup> weight loss testing was not possible as part of their effort because the nature and locations of the precipitator corrosion had not been defined. They recommended installation of corrosion coupons at appropriate locations within precipitators, ductwork and stacks based on their survey results and experience at the specific installation. They proposed collection and recording on a regular, periodic basis, of environmental conditions such as flue gas temperatures, dewpoints, SO<sub>2</sub> and TRS concentrations, gas velocities and black liquor sulfidity during the coupon exposure period. These would be compared with actual precipitator corrosion during the coupon exposure period.<sup>1,3</sup> They concluded their corrosion survey by noting that a more complete understanding of the chemistry of recovery boiler precipitator corrosion (i.e., the complex nature and interaction of the acid gases, salt cake particulate, and materials) is required.<sup>1</sup>

Some previous investigations of dewpoint corrosion in other industries have been described in the literature. This section highlights some of the methods using novel apparatus. Kear<sup>41</sup> has described a constant temperature corrosion probe. It was cooled with various coolants at the temperature of the boiling point of each one. The weight loss of an end element is measured. It could be used only for short tests when corrosion rates reach a maximum on a clean surface.

Dawson<sup>19</sup> noted that an air cooled metal corrosion probe may be useful in determining the corrosivity of gas streams. The probe comprises an hemispherical metal end piece which is cooled internally by air. Surface temperature is measured by a thermocouple. After a couple of hours the probe is

removed and corrosion rate determined by weight loss. This method does not duplicate conditions in the ESP and will not provide actual corrosion rates. However, it may provide relative comparisons of various exposure conditions. A similar design has been illustrated by Cox.<sup>14</sup> It has 6 one-inch diameter coupons flush mounted in a probe assembly. The coupons are electrically isolated and cooled from the back.

Dawson and coworkers<sup>19</sup> have described an electrochemical probe for monitoring corrosion under thin condensed electrolyte films. These probes consisted of a series of mild steel strips each insulated from its neighbors but with each alternate strip wired together. The electrodes were encapsulated so that one of the edges was exposed to the condensing flue gas. Air cooling of the back surface allowed temperature control of the exposed surface via a thermocouple. The distance between adjacent strips was sufficient to prevent bridging by deposits but was capable of retaining any condensed liquid film. To determine corrosion rates, they performed electrochemical impedance tests (in which an external AC perturbation was applied) and electrochemical noise measurements (using the observed fluctuations in corrosion potential and corrosion current which occur spontaneously when a metal corrodes). They claim that a combination of methods is best. They also used coupons and insert probes and briefly mention development of a spirally wound electrical resistance probe.

Commercially available electrical resistance probes (e.g., Rohrback) may be used to measure corrosion rates. These probes may not detect short-term effects. Erroneous results could be obtained owing to a difference in temperature between the exposed and reference elements, particularly when thermal changes are occurring during startups and so on.

In their test program, Dawson and coworkers<sup>19</sup> have found that corrosion mechanisms vary with each plant situation and that monitoring is a valuable aid in future design, problem diagnosis and life prediction. The development and application of systems for measuring corrosion rates in ESP's in the pulp and paper industry will yield similar rewards.

## CONCLUSIONS

Corrosion of electrostatic precipitators is a serious problem in the pulp and paper industry, costing considerable sums for maintenance and replacement. There is plenty to do before the corrosion problem can be controlled. Firstly, there is a need to better define the mechanism of corrosion. Secondly we must determine how the process causes corrosion. What are optimum conditions to avoid corrosion? How does recovery boiler operation influence flue gas composition and in turn corrosion rates? There is a need to know what materials to use and to identify what design changes or modifications would be most effective. Instruments to measure dewpoint,  $\text{SO}_3$ , temperature and corrosion rates must be developed or demonstrated.

There are good opportunities for reducing corrosion costs. Furthermore, if flue gases can be monitored and minimum temperature conditions identified for acceptable corrosion rates, then substantial savings of heat energy can be realized.

ACKNOWLEDGMENT

The support for this work provided by the Fourdrinier Kraft Board Group is gratefully acknowledged.

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